Acknowledgment. We are indebted to the National Institutes of Health for support through Research Grant GM 29775. Funds for the AM-300 NMR spectrometer used in this work were provided by the NSF through instrument Grant CHE-8411172. The kind cooperation of Professors Kato and Dev in supplying spectra of epimukulol is gratefully acknowledged.

Registry No. **1**, 4128-17-0; **2**, 93787-91-8; **3**, 104465-85-2; **4**, 104465-86-3; **5**, 104465-87-4; **6**, 104465-88-5; **7**, 104465-89-6; **8**, 104465-90-9; **9**, 104465-91-0; **10**, 104487-53-8; (±)-**11**, 104465-92-1; (±)-**12**, 104528-78-1; (±)-**13**, 104465-93-2; (±)-**14**, 104528-79-2; (±)-**15**, 104465-94-3; (±)-**16**, 104465-95-4; (±)-**17**, 104465-96-5; (±)-**18**, 59686-16-7; (±)-**19**, 104465-97-6; (±)-**20**, 104595-99-5; (±)-**21**, 92214-89-6; $(i\text{-Pr})_3SiC{\equiv}CCH_2Br$, 104465-98-7.

Supplementary Material Available: IR and ^{1}H NMR spectral data for **4**, **5**, **7–13**, and **15–21** (4 pages). Ordering information is given on any current masthead page.

James A. Marshall,* Todd M. Jenson
Bradley S. DeHoff

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

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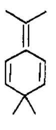
Crisscross Dimerization of 1-Isopropylidene-4,4-dimethyl-2,5-cyclohexadiene

Summary: Treatment of 1-isopropylidene-4,4-dimethyl-2,5-cyclohexadiene (1) with acid in the presence of trifluoroacetic anhydride and trifluoroacetic acid causes efficient formation of the dimer 3,10-bis(1-methylethylidene)-6,6,12,12-tetramethylpentacyclo[6.3.1.0^{2,7}.0^{4,11}.0^{5,9}]dodecane (2), a structural transformation without precedent in the absence of transition metals.

Sir: We report here that the substituted dendralene[1] 1-isopropylidene-4,4-dimethyl-2,5-cyclohexadiene[2] (**1**) can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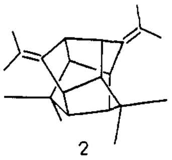
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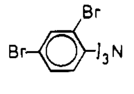
be efficiently converted to its crisscross dimer **2** in a single operation, in which four σ bonds form to generate four five-membered rings. We initially studied **1** to see if cation–radical-catalyzed oxygenation would occur, as it does with some methyl-substituted alkenes to give dioxetanes[3]. Cyclic voltammetry on **1** in 0.1 M $TBABF_4$ in CH_2Cl_2 with trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) (20:1:1 by volume) diplayed a partially reversible wave at a potential of 1.3 V vs. SCE, so formation of 1^+ with the one-electron oxidant $3^+SbCl_6^-$ is exothermic by 8 kcal/mol. When **1** was treated with 3^+ in the 20:1:1 solvent, the green color of 3^+ was discharged rapidly even at low temperatures, and **1** was consumed, but no oxygenation occurred. The products observed were formed both in the presence and in the absence of oxygen, so reaction of oxygen with 1^+ is slower than the observed chemistry to be reported.

The nonpolymeric products observed from **1** upon treatment with 3^+ are the acid-catalyzed rearrangement product 3,4-dimethylcumene (**4**), the dehydro dimer octamethylbicumyl (**5**), and a nonaromatic cage dimer,



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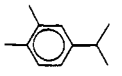
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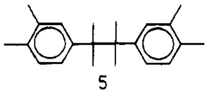
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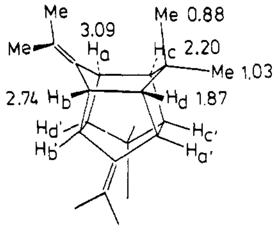
identified as 3,10-bis(1-methylethylidene)-6,6,12,12-tetramethylpentacyclo[6.3.1.0^{2,7}.0^{4,11}.0^{5,9}]dodecane (**2**). High resolution mass spectroscopy established the empirical formula of **2** as $C_{22}H_{32}$, yet it shows 11 carbons by ^{13}C NMR (δ 138.4, 115.4 [C_q, vinyl]; 39.3 [C_q]; 56.2, 55.6, 45.5, 45.3 [CH]; 31.0, 20.8, 20.09, 20.05 [CH_3]), so it must have a symmetry element despite the fact that both symmetry planes of the starting material **1** have been lost. Its ^{1}H NMR spectrum shows four methyl singlets, δ 1.61, 1.60 (assigned as $Me_2C[sp^2]$) and 1.03, 0.88 ($Me_2C[sp^3]$), and four non-first-order CH multiplets at 3.09 (H_a) and 2.74 (H_b) (assigned as allylic hydrogens) and 2.20 (H_c) and 1.87 (H_d) (assigned as nonallylic hydrogens). Both endocyclic vinyl groups of triene **1** are lost in going to the dimer, but the exocyclic $Me_2C{=}C$ unit appears to be intact. Both



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the ^{13}C and ^{1}H NMR spectra are uniquely consistent with the crisscross dimeric structure shown for **2**. We assign the upfield methyl group and the upfield allylic and nonallylic CH hydrogens (H_b and H_d, respectively) as those forced to lie in the shielding cone of the $Me_2C{=}C$ groups. The proton coupling constants, as well as the shielding cone argument, are only consistent with this assignment. The vicinal dihedral angles at the HCCH units which are about horizontal in the view shown are forced to be nearly 0°, while those held near vertical are about 30°, and must have a smaller J value. Decoupling experiments show that J_{ac} and J_{bd} are about 9 Hz, while $J_{ad'}$ is about 5.5 Hz, as expected from the Karplus $\cos^2\theta$ relationship. The non-first-order envelopes of H_a and H_d are nearly identical (largest absorption in the middle of the pattern), as are those of H_b and H_c (largest absorption displaced from the middle of the pattern), as is required by the diagonal relationships across the cage of **2**. The H_a and H_d multiplets have an extra expressed coupling compared to the H_b and H_c multiplets; the 30° vicinal hydrogen to H_b is $H_{b'}$ and to H_c is $H_{c'}$. In addition, the nearly perfect W plan ^4J couplings J_{ab} and J_{cd} are about 3 Hz, clearly larger than the non-W plan ^4J couplings $J_{ac'}$ and $J_{bd'}$. A 2D-COSY experiment showed that the two ^5J couplings J_{bc} and $J_{bc'}$ are completely absent, which is remarkable in such a cage structure; even couplings between the vinyl and aliphatic methyl groups could be clearly detected in this experiment. We argue that the C_2 symmetry present in the dimer and the pattern of chemical shifts and couplings observed makes our NMR assignment as **2** secure. This material is very difficult to crystallize, and X-ray quality crystals have not been obtained, although **2** slowly formed a waxy solid upon standing.

The relative amounts of **2**, **4**, and **5** observed are extremely sensitive to the reaction conditions. Considerable

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[1] Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 948.

[2] **1** was synthesized by the Wittig reaction of 4,4-dimethyl-2,5-cyclohexadienone and isopropylidenetriphenylphosphorane.

[3] (a) Nelsen, S. F.; Kapp, D. L.; Teasley, M. F. *J. Org. Chem.* **1984**, *49*, 579. (b) Nelsen, S. F.; Teasley, M. F. *Ibid.* **1986**, *51*, 3221.

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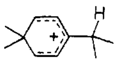
amounts of an insoluble white material which we assume is polymer were formed at lower concentrations and were removed by filtration through alumina before analysis of the products. **4** is obviously an acid-catalyzed rearrangement product of **1** and is formed efficiently when **1** is treated with acids such as TFA at room temperature. In neat CH_2Cl_2, dropwise addition of $3^+SbCl_6^-$ to 0.067 M **1** at −78 °C required 5.6 mol % oxidant before starting material was consumed, as indicated visually by the persistance of the green color of 3^+, and only cumene **4** was isolated after removal of polymer. Addition of 1% each of TFAA and TFA to the solvent (100:1:1) caused **2** and **5** to appear along with **4** in roughly similar amounts, ^1H NMR integration giving 30%, 40%, and 30%, respectively. Careful control of the conditions led to substantial improvement in the yield of **2**. Treatment of 0.5 M **1** in 100:10:1 CH_2Cl_2/TFAA/TFA at −86 °C required 12 mol % 3^+ to consume **1**, and workup gave a 12% loss of material, presumably as polymer. The product ratios by ^1H NMR were 77% **2**, 18% **4**, and 5% **5**, corresponding to a 68% crude yield of **2**. Pure **2** was obtained by preparative TLC in 57% yield. If **1** is subjected to the reaction conditions without 3^+, it is recovered unchanged. Thus it appeared that dimerization of **1** to **2** was catalyzed by one-electron oxidation conditions. Acid catalysis for the formation of **2** was, however, established by the proper control experiment. Treatment of 0.3 M **1** in 100:10:1 CH_2Cl_2/TFAA/TFA at −86 °C with HBF_4–Et_2O gave an 80% yield of **2** after preparative TLC; 12% **4** was observed but no **5** was detected. Control experiments established the need for TFA and TFAA in the reaction mixture to obtain **2**; only **4** was observed in their absence. We believe it noteworthy that **5** appears only under cation radical conditions. Its formation from 1^+ entails bonding between the terminal CMe_2 groups (a "radical" reaction), two methyl group shifts, and two deprotonations ("carbonium ion" reactions), producing acid which catalyzes the production of **2** and **4**, if enough acid for this purpose is not inadvertently introduced along with the 3^+.[4] We have no information on the timing of the bond formations and cleavages.

Protonation of **1** presumably gives pentadienyl cation **6**, which rearranges to produce **4** in the absence of trifluoroacetate groups but goes on to give **2** in their presence, for reasons that are as yet unknown. **6** could react with **1** by a concerted [4 + 2] cycloaddition[5,6] to give the diene–allyl cation intermediate **7**. Such additions are well-established for 2,5-cyclohexadienone derivatives, but we are unaware of any examples for hydrocarbons. Closure of **7** to **2** might involve stepwise [2 + 2] cycloaddition of its alkene and allyl cation fragments, which has limited precedent,[6,7] followed by deprotonation of the resulting tertiary cation. A particularly interesting feature of the production of **2** is that whether the cage structure can be produced has already been determined by the first cycloaddition, where formation of the endo intermediate **7** is apparently substantially favored over the exo form. The steric interactions of the gem-4,4-dimethyls with the six-membered rings in the transition-state complex of **1** and **6** would inhibit formation of the exo isomer. There is very little precedent for the conversion of **1** to its crisscross dimer **2**. The closest structural analogy we have found is the dimerization of norbornadienes[8] to analogous crisscross dimers in transition-metal-catalyzed (Fe, Rh) reactions which go in low yield.[9]



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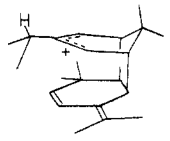

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Registry No. 1, 63577-41-3; 2, 104423-54-3; $3^+SbCl_6^-$, 58047-17-9; 4, 4132-77-8; 5, 104423-55-4.

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[4] (a) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. (b) Gassman, P. G.; Singleton, D. A. *Ibid.* **1984**, *106*, 7993.

[5] Walls, F.; Padilla, J.; Joseph-Nathan, P.; Giral, F.; Escobar, M.; Romo, J. *Tetrahedron* **1966**, *22*, 2387.

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[7] Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1.

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[9] **Acknowledgement**: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Amoco Oil Company for partial financial support of this research. We thank Dr. Bruce Adams for help with high field NMR experiments and the referees for encouraging us to reconsider acid catalysis for the production of 2.

Stephen F. Nelsen,* Mark F. Teasley
S. M. McElvain Laboratories
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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Electrochemical Glycosylation Method

Summary: Hydroxyl-protected and -unprotected glycosyl aryloxides react with alcohols under mild electrolytic conditions to give the corresponding glycosides.

Sir: Glycosylation of alcohols has conventionally been achieved by heterolysis of glycosyl derivatives having an anomeric leaving group (Gly-X) with Brønsted or Lewis acid promoters (eq 1).[1] Besides such two-electron exchange processes, cleavage of Gly–X bond stimulated by a one-electron-transfer process is an attractive alternative for this purpose. Equation 2 outlines the possible $S_{ON}1$ pathway[2] involving one-electron-oxidized substrates. Described herein is the first electrochemical method based on such strategy.[3,4]

$$\text{Gly-X} \xrightarrow{-X^-} \text{Gly}^+ \xrightarrow{\text{ROH}} \text{Gly-OR} \qquad (1)$$

$$\text{Gly-X} \xrightarrow{-e} \text{Gly-X}^{\bullet+} \xrightarrow{-X^\bullet} \text{Gly}^+ \xrightarrow{\text{ROH}} \text{Gly-OR} \qquad (2)$$

When electricity was passed through a mixture of an *aryl* glycoside (**1**), alcoholic nucleophile (1:1 to 1:2 molar ratio), and electrolyte in an appropriate polar solvent placed in an undivided cell under a constant voltage by

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[1] Pertinent reviews: Wulff, G.; Röhle, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 157. Igarashi, K. *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 243. Bochkov, A. F.; Zaikov, G. E. *Chemistry of the O-Glycosidic Bond: Formation and Cleavage*; Pergamon: Oxford, 1979. Tsutsumi, H.; Ishido, Y. *J. Synth. Org. Chem. Jpn.* **1980**, *38*, 473. Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Koto, S.; Morishima, N.; Zen, S. *J. Synth. Org. Chem. Jpn.* **1983**, *41*, 701.

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